

# An ab-initio evaluation of the local effective interactions in the superconducting compound $\text{Na}_{0.35}\text{CoO}_2 - 1.3\text{H}_2\text{O}$

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We used ab-initio quantum chemical methods, treating explicitly the strong correlation effects within the cobalt  $3d$  shell, as well as the screening effects on the effective integrals, for accurately determining on-site and nearest-neighbor (NN) interactions in the  $\text{Na}_{0.35}\text{CoO}_2 - 1.3\text{H}_2\text{O}$  superconducting compound. The effective ligand field splitting within the  $t_{2g}$  orbitals was found to be  $\delta \sim 300$  meV, the  $a_{1g}$  orbital being destabilized compared to the  $e'_g$  ones. The effective Hund's exchange and Coulomb repulsion were evaluated to  $J_H \sim 280$  meV and  $U \sim 4.1\text{--}4.8$  eV for the  $a_{1g}$  orbitals. The NN hopping parameters were determined within the three  $t_{2g}$  orbitals and found to be of the same order of magnitude as the  $t_{2g}$  ligand field splitting. This result supports the hypothesis that a three band model would be better suited than a one-band model for this system. Finally we evaluated the NN effective exchange integral to be antiferromagnetic and  $J = -66$  meV.

## I. INTRODUCTION

The layered cobalt oxides have been attracting a lot of attention for the last few years. This interest is driven by the remarkable properties of the  $\text{Na}_x\text{CoO}_2$  compounds and more specially their hydrated counterpart. Indeed, superconductivity was discovered in the  $\text{Na}_{0.35}\text{CoO}_2 - 1.3\text{H}_2\text{O}$ <sup>1</sup>, for the first time in layered oxides, beside its discovery in the cuprates.

The host material is composed of  $\text{CoO}_2$  layers, where the cobalt atoms are located in distorted edge-sharing octahedra forming a two-dimensional triangular lattice. The sodium atoms are located in a plane in between the  $\text{CoO}_2$  layers. In the hydrated superconducting material, the water molecules are intercalated in between the sodium and the cobalt oxide layers. The water intercalation is fragile and the system loses its water out of a hydrated atmosphere. It seems however, that at low temperature, the water and sodium cations order in a two-dimensional super-cell and adopt a frozen local geometry similar to clusters of  $\text{Na}^+$  ions embedded in ice<sup>2</sup>. Despite this possible ordering, it is believed that the effect of the water molecules is only steric<sup>1</sup>. Indeed, the water inclusion induces a large separation of the  $\text{CoO}_2$  layers, responsible for essentially uncoupled cobalt layers and a two-dimensional physics<sup>3</sup>. This two-dimensional character is assumed to be necessary for superconductivity to occur.

A simple formal charge analysis shows that the cobalt ions are  $3.65+$  for  $x = 0.35$ , that is about one third of  $\text{Co}^{3+}$  ions and two third of  $\text{Co}^{4+}$  ions. Wet-chemical redox analyses revealed however a cobalt oxidation number somewhat lower<sup>4</sup> :  $3.46+$ , that is closer to half  $\text{Co}^{3+}$ , half  $\text{Co}^{4+}$  ions. The distortion of the  $\text{CoO}_6$  octahedra observed in the superconducting material corresponds to a compression along the  $x + y + z$  axis of the Co coordination octahedron. This trigonal distortion induces a lowering of the  $O_h$  local point group to a  $d_3$  subgroup, thus splitting the  $t_{2g}$  orbitals in a  $a_{1g}$  and two  $e'_g$  ones (see figure 4 in the results section). Authors however

disagree on the relative energies of the orbitals and the amplitude of the splitting. While some authors<sup>5</sup> support the idea that the  $a_{1g}$  orbital is lowered compared to the two  $e'_g$ , other authors come to the opposite conclusion<sup>6</sup>. Density functional Theory (DFT) calculations<sup>7</sup> agree on the fact that the  $a_{1g}$  band is less filled than the ones originating from the  $e'_g$  orbitals. However, the relative energies of the different atomic configurations are not directly accessible to DFT calculations. Indeed, electronic correlation is assumed to be very strong in this system and can be expected to strongly influence the local atomic excitation energies between the different configurations associated with the hole localization either on the  $a_{1g}$  or on one of the two  $e'_g$  cobalt atomic orbitals. The question of the relative energy of these different configurations is however crucial in order to determine the pertinent degrees of freedom to be taken into account in a simple model, able to describe the low energy properties of the system. Indeed, assuming that the  $a_{1g}$  orbital is much higher in energy than the  $e'_g$  ones, one should naturally conclude that the pertinent model for the description of the superconductivity is a one band  $t - J$  type of model. Assuming that the  $a_{1g}$  orbital is now much lower in energy than the  $e'_g$  ones, one comes to a two-band model, while if the three orbitals are only weakly split, the pertinent model should consider all of them at the time. No consensus is reached nowadays in the literature and there is a large controversy on the pertinent model to consider.

The aim of the present paper is to determine the local orbital energies and effective coupling parameters between the cobalt  $3d$  orbitals. For this purpose we used embedded clusters calculations and quantum chemical ab-initio methods treating exactly the correlation effects within the  $3d$  shell as well as the screening effects that renormalize the interactions. Such methods allow the direct computation of the local parameters such as the atomic effective ligand field splitting, the one-site Hubbard  $U$  coulombic repulsion as well as the Hund's exchange. In addition, nearest neighbor exchange and transfer interactions can be directly and accurately com-

puted.

The next section will shortly describe the method, section three will relate the results and finally the last section will be devoted to discussion and conclusion.

## II. METHOD AND COMPUTATIONAL DETAILS

The method used in this work (CAS+DDCI<sup>8</sup>) is a configurations interaction method, that is an exact diagonalisation method within a selected set of Slater determinants, on embedded crystal fragments. This method has been specifically designed to accurately treat strongly correlated systems, for which there is no single-determinant description. The main point is to treat exactly all correlation effects and exchange effects within a selected set of orbitals (here the  $3d$  shell of the cobalt atoms) as well as the excitations responsible for the screening effects on the exchange, repulsion, hopping, etc. integrals.

The CAS+DDCI method has proved very efficient to compute, within experimental accuracy, the local interactions (orbital energies, atomic excitations, exchange and transfer integrals, coulomb repulsion etc.) of a large family of strongly correlated systems such as high  $T_c$  copper oxides<sup>9</sup>, vanadium oxides<sup>10</sup>, nickel and cuprate fluorides<sup>11</sup>, spin chains and ladders<sup>12</sup>, etc.

The clusters used in this work involve either one cobalt ( $\text{CoO}_6$ ) or two cobalt atoms ( $\text{Co}_2\text{O}_{10}$ ) and their oxygen first coordination shell (see figure 1). These fragments are embedded in a bath designed so that to reproduce on them the main effects of the rest of the crystal ; that is the Madelung potential and the exclusion effects of the electrons of the other atoms of the crystal on the clusters electrons.

The electrostatic potential is reproduced by a set of point charges located at the atomic positions. The charges are renormalized next to the bath borders in order to obtain an exponential convergence of the Madelung potential. The convergence accuracy was set in the present work to the mili-electron-Volt. The method used for this purpose is a generalization<sup>13</sup> of the Evjen's method<sup>14</sup>. The nominal atomic charges used in this work are the formal charges, that is  $+3.65$  for the cobalt atoms,  $-2$  for the oxygen atoms and  $+1$  for the sodium atoms. The sodium atoms being located at two crystallographic sites, with fractional occupations, we renormalized the associated charges with the crystallographic occupation, thus using a mean field averaging of the Madelung potential. At this point we would like to shortly discuss the question of the Co valency and insertion of  $[\text{H}_3\text{O}]^+$  ions. Indeed, it is clear that both the  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  atomic configurations of the Co atom are present in the system, however the actual average charge supported by the cobalt is under debate. A modification of the cobalt average charge would act on our calculations through a modification of the electrostatic potential seen by the

computed cluster. A global shift of the electrostatic potential seen by the cluster would of course have no effects on our results. However, a relative shift of the electrostatic potential seen by the cobalt and oxygen atoms would have a strong effect. Indeed, a reduction of the potential difference between the bridging oxygen orbitals and the cobalt magnetic orbitals can be expected to increase the effective exchange integrals through the lowering of the ligand-to-metal charge transfer configurations that mediate the interactions. On the contrary, an increase of the potential difference between these orbitals would decrease the effective exchange.

The exclusion effects are treated using total ions pseudo-potentials<sup>15</sup> (TIP) on the first shell of atomic sites surrounding the clusters.

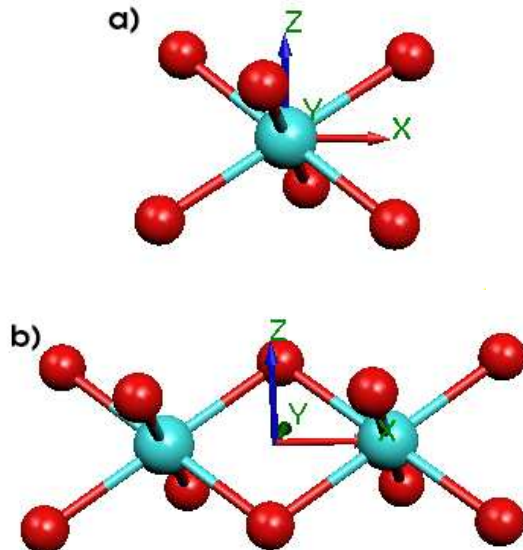


FIG. 1: a)  $\text{CoO}_6$  and b)  $\text{Co}_2\text{O}_{10}$  clusters used in the present calculations.

In this description the water molecules are not explicitly considered. Indeed, we supposed correct the usual idea that their role is only the increase of the  $c$  parameter, uncoupling the  $\text{CoO}_2$  layers. This point is correctly treated in our calculations since the atomic positions (both in the quantum clusters and in the baths) are taken as given in the crystallographic data. One could argue that the water molecules should be taken into account in the clusters environment, however since water do not present a total net charge but only a dipole moment, its effect is expected to be very small. We thus neglected this aspect.

The calculations presented in this work are specific for the hydrated compound. In the dehydrated  $\text{Na}_{0.35}\text{CoO}_2$  phase, the atomic positions differ from the one used here, and more specifically the  $\text{CoO}_2$  inter-layers distances are strongly reduced. Even if the atomic fractional positions were not changed by the dehydration, the electrostatic potential seen by the cobalt and oxygen atoms of the

CoO<sub>2</sub> layers would be strongly modified and thus the different orbital energies (and other parameters) would be affected. Whether one would like to perform calculations for other sodium concentrations, adequate structural data as well as cobalt average valency should be taken.

The calculations were done using the MOLCAS<sup>16</sup> and CASDI<sup>17</sup> set of programs. The basis sets used can be found in reference<sup>18</sup>. The structural parameters were taken from the Nature paper of Takada<sup>1</sup>.

### III. RESULTS

As mentioned in the previous section we performed two sets of calculations. The first one aimed at determining the one-site effective parameters such as the cobalt 3*d* energy splitting due to the ligand field. This orbital splitting is renormalized by the correlation effects within the 3*d* shell as well as by the screening effects due to the virtual excitations. The second type of calculations aimed at determining the Co–Co interactions, transfer between the different 3*d*, former *t*<sub>2*g*</sub>, orbitals as well as the effective exchange integrals.

#### A. The effective on-site 3*d* energy splitting

Calculations with a formal Co<sup>4+</sup> cation were performed on the embedded CoO<sub>6</sub> cluster. Figure 3 reports the first excitation energies and the dominant term of the associated wave functions. Figure 2 shows the Co atomic orbitals.

One sees immediately that the *a*<sub>1*g*</sub> orbital is a 3*d*<sub>*c*<sup>2</sup>−*r*<sup>2</sup></sub> orbital in the **a**, **b**, **c** crystallographic axes. As stated in many papers it can be written in as

$$d_{c^2-r^2} = (d_{xy} + d_{xz} + d_{yz}) / \sqrt{3}$$

if *x*, *y*, *z* are the Co–O nearly orthogonal directions of the CoO<sub>6</sub> octahedron. As expected the three low energy orbitals are pointing between the oxygen atoms, while the high energy ones are directed toward the ligands. Another important point to notice is the amount of Co(3*d*)–O(2*p*) hybridization in the cobalt orbitals. Indeed, while the two *e*<sub>*g*</sub>' orbitals do not present noticeable delocalization on the neighboring oxygen ligands, the *a*<sub>1*g*</sub> orbital exhibits some mixing with the oxygen 2*p*<sub>*z*</sub> orbitals — namely about 2/3 Co(3*d*) and 1/3 O(2*p*) — and the two *e*<sub>*g*</sub> orbitals are strongly hybridized with the oxygen 2*p* with for the two *e*<sub>*g*</sub> about 55% Co(3*d*) and 42% on the O(2*p*).

Figure 3 shows us that in the ground state, the hole is located on the *a*<sub>1*g*</sub> orbital, which is destabilized compared to the *e*<sub>*g*</sub>'. Figure 4 pictures this result as the effective ligand field splitting associated with the trigonal distortion. This result is in agreement with the finding of the different DFT ab initio calculations. It however disagrees with

the ligand field analysis of reference<sup>5</sup>. It is well known that when the transfer (overlap) between a 3*d* metal orbital and the occupied ligand orbitals increases, the metal 3*d* orbital is destabilized. This can be seen in a simple tight binding picture between a metal 3*d* and ligand 2*p* orbitals. At the second order of perturbation, the metal 3*d* orbital is destabilized by the quantity  $t^2/(\varepsilon_d - \varepsilon_p)$  while the ligand 2*p* orbital is stabilized by the same value, due to their hybridization. This is presently the case, since the apex oxygens approach the cobalt plane in the distorted tetrahedron, and thus the overlap between the *a*<sub>1*g*</sub> cobalt orbital and the oxygen 2*p* orbitals is slightly augmented. The computed resulting effective orbital energy splitting is of the order of 300 meV as can be seen on figure 3, that is in global agreement with — even if somewhat larger than — the LDA+U estimation<sup>19</sup> (0.2 eV) from the top of the *a*<sub>1*g*</sub> and *e*<sub>*g*</sub>' bands. Finally, one should notice a further splitting between the *e*<sub>*g*</sub>' orbitals themselves. This very small splitting is due to the fact that the electrostatic field generated by the sodium cations on the cobalt does not present a perfect three-fold symmetry. This value is however very small and can be neglected for any practical purpose.

The *a*<sub>1*g*</sub>–*e*<sub>*g*</sub> splitting can be extracted from the Co atomic *d* → *d* excitations of higher energies. Typically the *S* = 3/2 and *S* = 5/2 states should be computed. We found a *a*<sub>1*g*</sub>–*e*<sub>*g*</sub> splitting of 1.8eV and thus a *e*<sub>*g*</sub>'–*e*<sub>*g*</sub> splitting of 2.1eV, in global agreement with the LDA evaluations of 2.5eV<sup>20</sup>.

#### B. The inter-atomic interactions

As mentioned in the introduction, one of the open questions in the modeling of the present compound is whether only the *a*<sub>1*g*</sub> band is important for the physical properties or whether one should consider a multi-band model. Indeed, Lee *et al*<sup>20</sup> proposed from LDA+U calculations that a crossover occurs between a single band behavior and a three band behavior as a function of the band filling. For an equivalent sodium concentration *x* < 0.5 they suggest a three band model and for *x* > 0.5 a single band one. On the model point of view, while several authors argue, on analytical as well as numerical results, that proper superconductivity behavior cannot be found using a single band *t* – *J* type model<sup>21</sup>, other authors found superconducting pairing within a single band *t* – *J* model<sup>22</sup>.

In order to address this question one should be able to accurately evaluate the effective transfer and exchange integrals between the three former *t*<sub>2*g*</sub> → 2*e*<sub>*g*</sub>' + *a*<sub>1*g*</sub> orbitals. It is crucial in their evaluation to properly take into account all Coulomb repulsions, exchange and screening effects, as well as the metal–ligands charge transfers.

These effective transfer integrals between two nearest neighbor cobalt atoms can be extracted from the first electronic excitations of an embedded Co<sub>2</sub>O<sub>10</sub> cluster

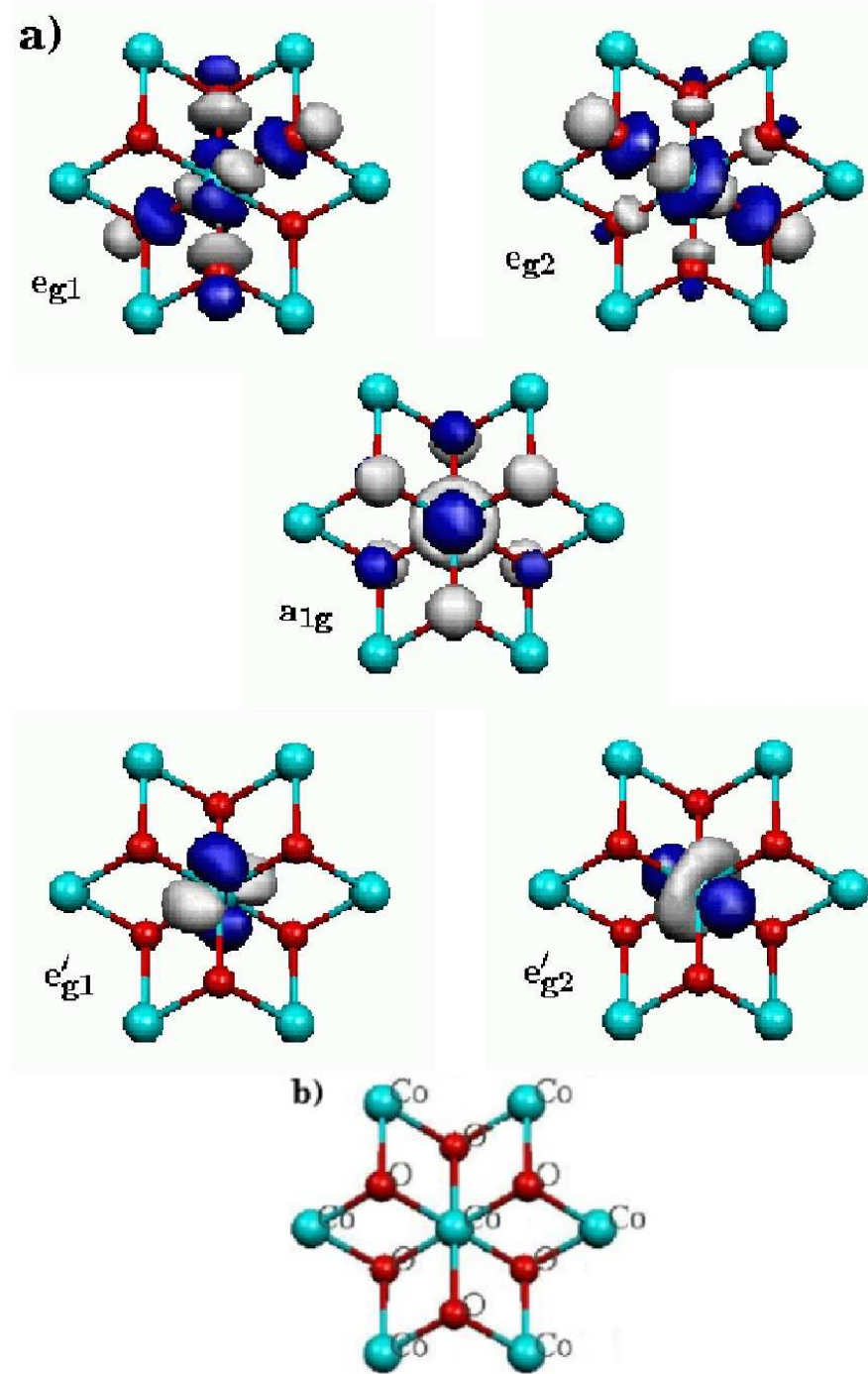


FIG. 2: a)  $Co^{4+}$  orbitals in the  $Na_{0.35}CoO_2 - 1.3H_2O$  compound. b) Label of the different atoms. The c axis is orthogonal to the figure plane.

with  $Co^{3+} - Co^{4+}$  mixed cobalt valency. The computed lowest six states can be associated with symmetric and antisymmetric combinations of the atomic states shown in figure 3. As mentioned earlier, the effective transfer integrals are strongly mediated by the oxygen 2p orbitals. Figure 5 shows the oxygen 2p orbitals bridging the Co - Co interactions. One can write the following matrix in-

teraction between the cobalt  $a_{1g}$  and  $e'_g$  3d orbitals and

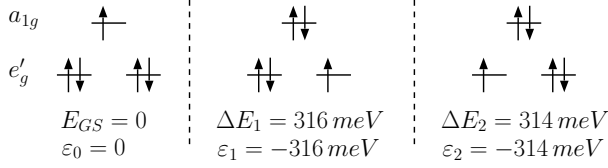


FIG. 3: Schematic representation of the ground and first excited states of the  $\text{Co}^{4+}$  ions in the  $\text{Na}_{0.35}\text{CoO}_2 - 1.3\text{H}_2\text{O}$  compound and corresponding excitation energies.

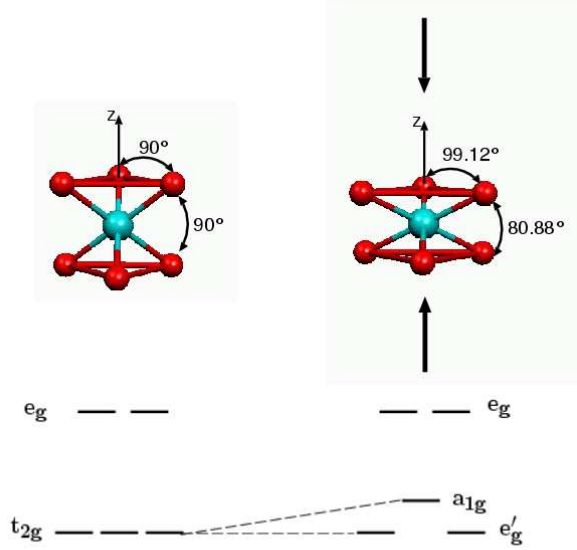


FIG. 4: Schematic representation of the trigonal distortion ligand field splitting as found from the ab initio correlated calculations. Angles in the distorted structure correspond to the atomic positions given in reference<sup>1</sup>.

the bridging oxygen  $2p$  ones

$$\begin{pmatrix}
 a_{1g}^l & e_{g1}^l & e_{g2}^l & a_{1g}^r & e_{g1}^r & e_{g2}^r & 2p_z & 2p_1 & 2p_2 \\
 \varepsilon_0 & & & & & & & & \\
 0 & \varepsilon_1 & & & & & & & \\
 0 & 0 & \varepsilon_2 & & & & & & \\
 t_{00}^d & 0 & t_{20}^d & \varepsilon_0 & & & & & \\
 0 & t_{11}^d & 0 & 0 & \varepsilon_1 & & & & \\
 t_{20}^d & 0 & t_{22}^d & 0 & 0 & \varepsilon_2 & & & \\
 t_{0p_z} & 0 & t_{2p_z} & t_{0p_z} & 0 & t_{2p_z} & \varepsilon_{p_z} & & \\
 0 & t_{1p_1} & 0 & 0 & t_{1p_1} & 0 & 0 & \varepsilon_{p_1} & \\
 t_{0p_2} & 0 & t_{2p_2} & t_{0p_2} & 0 & t_{2p_2} & 0 & 0 & \varepsilon_{p_2}
 \end{pmatrix}$$

where the  $l$  and  $r$  superscripts are associated with the two cobalt atoms, the  $\varepsilon_i$  diagonal energies are the effective orbital energies,  $t_{ip_j}$  are the cobalt  $3d_i$ -oxygen  $2p_j$  transfers and the  $t_{ij}^d$  are the direct transfer integrals between the  $3d_i$  and  $3d_j$  orbitals of the two cobalt atoms. The direct integrals are small, however non negligible due

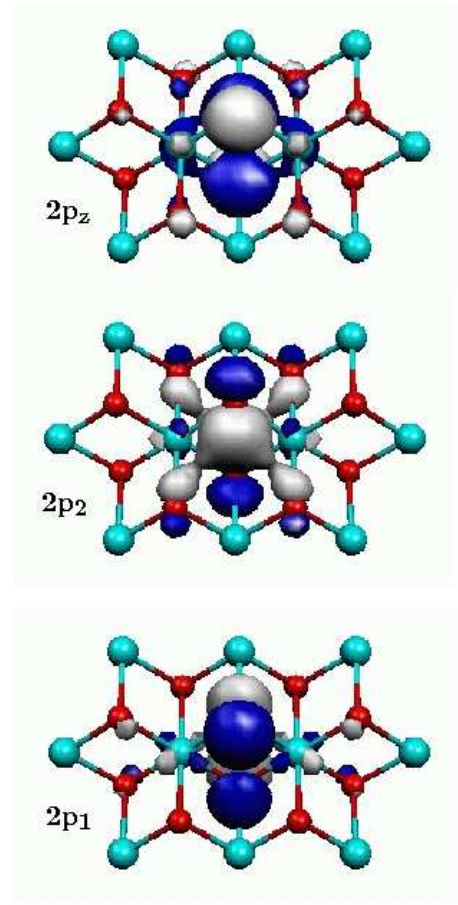


FIG. 5: Oxygen  $2p$  orbitals mediating the interactions between the  $a_{1g}$  and  $e_g'$  orbitals of the two Co atoms. One sees that the  $p_z$  and  $p_2$  orbitals overlap with both the  $a_{1g}$  and  $e_{g2}'$  cobalt orbitals, while the  $p_1$  overlap with the  $e_{g1}'$  cobalt orbitals.

to the short Co-Co distance and the  $p$ - $d$  hybridization as far as the  $a_{1g}$  orbitals are concerned. In fact the  $t_{22}^d$  direct transfer could be omitted, since this one is really very small. In addition, we will see later that we cannot explain our results without explicitly considering at least the  $t_{02}^d$  term. Such a  $3d - 2p$  model may be considered as a bit too complex for practical uses. In addition, a rapid analysis of the computed wave functions shows that the explicit contribution of the  $\text{O}(2p) \rightarrow \text{Co}(3d)$  excitations are quite small, even if very important for the mediation of the interactions between the two cobalt atoms. Indeed, the weight of these configurations is less than 4% in the wave functions. We can thus reduce the previous matrix into an effective Hamiltonian on the sole cobalt  $3d$  orbitals. All the effects of the oxygen  $2p$  orbitals should however be taken into account to properly describe the physics. It results the following effective Hamiltonian, where both inter-atomic and intra-atomic coupling terms

appear between the  $a_{1g}$  and  $e'_{g2}$  orbitals.

$$H_d = \begin{pmatrix} a_{1g}^l & e'_{g1}^l & e'_{g2}^l & a_{1g}^r & e'_{g1}^r & e'_{g2}^r \\ \varepsilon_0 & 0 & tp_{20} & t_{00} & 0 & t_{20} \\ 0 & \varepsilon_1 & 0 & 0 & t_{11} & 0 \\ tp_{20} & 0 & \varepsilon_2 & t_{20} & 0 & t_{22} \\ t_{00} & 0 & t_{20} & \varepsilon_0 & 0 & tp_{20} \\ 0 & t_{11} & 0 & 0 & \varepsilon_1 & 0 \\ t_{20} & 0 & t_{22} & tp_{20} & 0 & \varepsilon_2 \end{pmatrix} \quad (1)$$

where  $t_{ij}$  are the effective resulting transfer integrals (direct plus mediated by the oxygen ligands) between the  $3d_i$  orbital of one cobalt and  $3d_j$  of the other,  $tp_{02}$  is the intra-atomic  $a_{1g}$ - $e'_{g2}$  effective transfer resulting from the interactions with the oxygen  $2p$  orbitals. This last  $tp_{02}$  integral is in fact quite surprising since one does not expect such an intra-atomic effective transfer to take place. It however can easily be explained in perturbation theory. Figure 6 pictures the mechanism responsible for the effective transfers between the  $a_{1g}$  and  $e'_{g2}$  orbitals of the two cobalt atoms, mediated by one oxygen orbital. The fact that both the  $a_{1g}$  and  $e'_{g2}$  orbitals present non negligible transfer integrals toward the same oxygen  $2p$  orbitals result in the fact that four different configurations couple, at the second order perturbation theory, to the ground state of the  $\text{Co}^{4+}$ - $\text{Co}^{3+}$  ions. Indeed, one has the following expression for the effective transfers between the  $a_{1g}$  and  $e'_{g2}$  orbitals of the Co atoms

$$t_{00} = t_{00}^d - \frac{(t_{0p_z})^2}{\Delta_0} - \frac{(t_{0p_2})^2}{\Delta_0} \quad (2)$$

$$t_{20} = t_{20}^d - \frac{t_{0p_z}t_{2p_z}}{\Delta_{02}} - \frac{t_{0p_2}t_{2p_2}}{\Delta_{02}} \quad (3)$$

$$tp_{20} = -\frac{t_{0p_z}t_{2p_z}}{\Delta_{02}} - \frac{t_{0p_2}t_{2p_2}}{\Delta_{02}} \quad (4)$$

with  $\Delta_0 = \varepsilon_0 - \varepsilon_p + 5(U - 2J_H) - U_p$ , the  $\Delta_{02}$  denominator being in the Descloiseaux acception of the quasi-degenerate perturbation theory<sup>23</sup>

$$\frac{2}{\Delta_{02}} = \frac{1}{\Delta_0} + \frac{1}{\Delta_2}$$

with  $\Delta_2 = \varepsilon_2 - \varepsilon_p + 5(U - 2J_H) - U_p$ .

$U$  is the Coulomb repulsion for two electrons in the same Co  $3d$  orbital,  $J_H$  is the Hund exchange, and  $U_p$  is the Coulomb repulsion in the oxygen orbitals. Finally, the last term corresponds to a renormalization of the  $a_{1g}$  orbital energy

$$\varepsilon_0 \rightarrow \varepsilon_0 - \frac{(t_{0p_z})^2}{\Delta_0} - \frac{(t_{0p_2})^2}{\Delta_0} \quad (5)$$

Similarly the perturbation theory yields, at the second order, for  $t_{11}$  and  $t_{22}$

$$t_{11} = t_{11}^d - \frac{(t_{2p_1})^2}{\Delta_1}$$

$$t_{22} = t_{22}^d - \frac{(t_{2p_z})^2}{\Delta_2} - \frac{(t_{2p_2})^2}{\Delta_2}$$

with  $\Delta_1 = \varepsilon_1 - \varepsilon_p + 5(U - 2J_H) - U_p$ .

If the  $tp_{20}$  term is not included in the effective model, it is impossible to fit the computed wave functions and energies with a good accuracy. Of course, it is possible to rotate the orbitals in such a way to nullify the  $tp_{20}$  term. It would however result in a set of orbitals that would be i) bond dependent and ii) no more belonging to the irreducible representation of the whole system. Indeed, the axis of the  $a_{1g}$  orbital would for instance be tilted with respect to the  $\mathbf{c}$  axis in a direction dependent of the Co-Co direction. In order to keep a simple model, respecting the system symmetry, it appears better to us to use a non-zero  $tp_{20}$  term.

The quality of the model can be evaluated by two ways. The first criterion is the norm of projection of the computed wave functions on the configurations space associated with the model (model space). In the present case the model space is the six combinations of the atomic electronic states pictured in figure 3. Large norms warrant that the space supporting the model captures the physics of the system. In our calculations the minimal value obtained for the norms of the six projected wave functions is 0.87. The missing part of the computed wave function is composed by the excitations responsible for the screening effects that is more than 17 millions configurations in our calculation. Table I displays the effective transfer parameters obtained from the fit of  $H_d$ . The

Parameter	$t_{00}$	$t_{11}$	$t_{22}$	$t_{20}$	$t_p$
Value (meV)	-276	348	-12	-89	-53

TABLE I: Effective hopping parameters between former  $t_{2g} \rightarrow a_{1g} + 2e'_g$  orbitals.

present fit was done by fulfilling (at the best) the standard effective Hamiltonians requirements<sup>24</sup>; that is

- that the projection of the exact wave functions in the space supporting the effective Hamiltonian are eigenfunctions of the later,
- associated with the exact energies.

It results in the minimization over the  $H_d$  parameters of the following Lagrangian

$$\mathcal{L}^2 = \sum_m |H_d P \Psi_{exact}(m) - E_{exact}(m) P \Psi_{exact}(m)|^2$$

where  $P$  is the projection over the space supporting  $H_d$  and  $\Psi_{exact}(m)$  are the ab initio wave functions associated with the ab initio energies  $E_{exact}(m)$ . The quality of the fit is very good since the average error ( $\mathcal{L}/6$ ) can be evaluated to 1meV.

Let us now concentrate on the effective exchange integral  $J$  between the  $a_{1g}$  Fermi level orbitals.  $J$  can be evaluated from the singlet-triplet excitation energy on a  $\text{Co}_2\text{O}_{10}$  embedded cluster with two formally  $\text{Co}^{4+}$  ions.

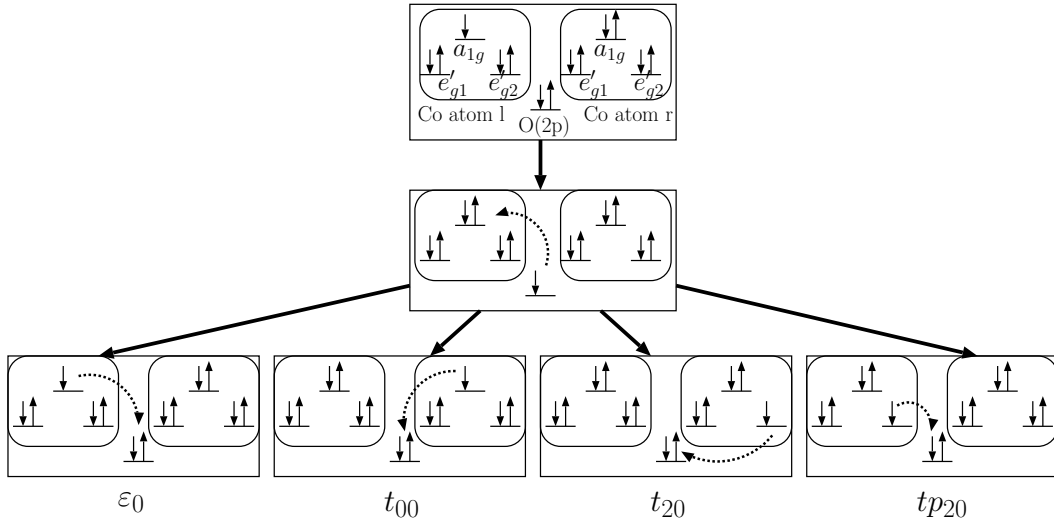


FIG. 6: Through bridge perturbative mechanism responsible for transfers between the  $a_{1g}$  and  $e'_{g2}$  orbitals of two nearest neighbor cobalt. The representation of the left and right Co atoms as well as the orbital denominators are given in the starting step. The arrows picture at each step the electron transfer yielding the present configuration. Under each configuration of the last step, the hopping or energy term to which it contributes is indicated. Analytic formula associated with the present picture can be found in the set of equations 2 to 5.

Our calculations yield an antiferromagnetic coupling, in agreement with the experimental findings<sup>25</sup> and LDA+U calculations for large  $U$  values<sup>20</sup>. The computed value is

$$J = -66\text{meV}$$

One should note that our evaluation of both the effective transfer and exchange integrals are larger than the LDA and even LDA+U evaluations found in the literature. This fact is due to the well known problem of the density functional methods to correctly treat strongly correlated systems. Indeed, it is well known that in numerous cases, the DFT results strongly overestimated the ferromagnetism, in particular in transition metal oxides where  $3d$  orbitals play an important role. This is in particular the case for the present compound since LDA finds, for all compositions from  $x = 0.3$  to  $x = 0.7$ , the system ferromagnetic and metallic, in disagreement with experimental results. LDA+U somewhat correct this problem, however only in a mean-field way, the quantum fluctuations due to the electronic correlation being ignored. In the present case, the authors of reference<sup>26</sup> show that the LDA+U method of incorporating correlation effects is ill-suited for the  $Na_xCoO_2$  family of compounds.

### C. One site bi-electronic repulsion and Hund's exchange

The effective Coulomb repulsion of two electrons in the same  $a_{1g}$  orbital,  $U$ , can be extracted from the present calculations in two different ways. On one hand,  $U$  can be evaluated from the ground-state energy difference between the  $Co^{3+}$  and  $Co^{4+}$  ions, embedded in the

$Na_{0.35}CoO_2 - 1.3H_2O$ . It yields  $U_1 = 4.1\text{ eV}$ . On the other hand,  $U$  can also be evaluated from the knowledge of both the hopping and exchange integrals between two nearest neighbor  $a_{1g}$  Co orbitals. Its value can thus be estimated to  $U_2 = 4.8\text{ eV}$ . One immediately notices that the first estimation is somewhat weaker than the second one. Let us analyze this discrepancy.

- The first value ( $U_1$ ) corresponds to a static increase of the cobalt charge, while the second ( $U_2$ ) corresponds to the energy of the quantum fluctuations :  $Co^{3+}-Co^{5+}$  in a globally  $Co^{4+}-Co^{4+}$  state. The Hubbard and related models use a unique parameter for these two concepts. As far as the raw repulsion integrals are concerned, there is indeed a unique  $U$ . However, screening effects act differently on the static  $Co^{3+}$  configuration leading to  $U_1$  and on the quantum  $Co^{3+}-Co^{5+}$  fluctuations leading to  $U_2$ . Indeed, it is well known in quantum chemistry that the static screening acting on  $U_1$  is quite larger than the dynamical one acting on  $U_2$ . It thus results in a smaller value for  $U_1$  compared to  $U_2$ .
- The  $U_2$  value corresponds in fact to the difference between the one site repulsion  $U$  and the repulsion  $V$  between the  $a_{1g}$  orbitals of nearest neighbor Co atoms. It means that the on-site repulsion responsible for the correct quantum fluctuations between two nearest neighbor is even larger than the computed  $U_2$  value. The  $4.8\text{ eV}$  value thus constitutes a lower bound for the repulsion responsible for the quantum fluctuations.



Even-though one cannot definitely conclude on the relative values of  $U$  and  $V$ , one can expect from the above analysis that the effective repulsion between nearest neighbor Co sites is probably small. The above  $U_2$  values were extracted for a one-band model. Whether one would like to use a three band model based on both the  $a_{1g}$  and the  $e'_g$  orbitals, one should take off the screening effects due to latters. This can be done in a perturbative manner. Indeed, the difference in the screening of the  $U_2$  parameter between the one-band and three-bands models can be evaluated to

$$U_2(1b) = U_2(3b) + \Delta$$

where  $U_2(1b)$  is the one-band  $U_2$  and  $U_2(3b)$  is the three-band one and

$$\Delta = -2\frac{t_p^2}{\delta - 2J_H} + 2\frac{t_p^2}{\delta} - 2\frac{t_{20}^2}{\delta - U} + 2\frac{t_{20}^2}{\delta - U - 2J_H} - 2\frac{J_H^2}{2\delta}$$

The on-site repulsion between two different  $3d$  orbitals  $U_{dd'}$  was taken in the classical way equal to  $U - 2J_H$ . Using the numerical values of the present work we find

$$\Delta = -193\text{meV} \quad \text{thus} \quad U_2(3b) = 5.0\text{eV}$$

Finally we would like to recall that the Coulomb repulsion in the  $a_{1g}$  orbitals was evaluated from soft X-ray photo-emission spectroscopy<sup>27</sup>. The cobalt core  $2p$  spectrum exhibits well separated  $\text{Co}^{4+}$  and  $\text{Co}^{3+}$  levels, consistent with a repulsion value in the range of  $U \sim 3\text{--}5\text{eV}$ , in total agreement with our calculations. Let us note that these values are somewhat weaker than the values usually taken in LDA+U calculations<sup>19,20,28</sup> ( $5 - 8\text{eV}$ ).

The Hund intra-atomic exchange integral,  $J_H$ , between the  $3d$  orbitals of the cobalt atom can be evaluated from the excitation energies between the ground state and the higher spin states ( $S = 3/2$ ,  $S = 5/2$ ) of the  $\text{Co}^{4+}$  ion. It comes  $J_H = 276\text{meV}$ , to be compared with the raw  $e'_g$ - $a_{1g}$  exchange integral of  $0.95\text{eV}$ . Hund's exchange

values are thus strongly renormalized by the screening effects in  $\text{Na}_{0.35}\text{CoO}_2 - 1.3\text{H}_2\text{O}$ , leading to the low-spin ground-state observed in the  $\text{CoO}_2$  layers. Indeed, the low-spin, high-spin excitation energy can be written as  $2(\varepsilon_{e_g} - \varepsilon_{e'_g}) - 10J_H$ . With a Hund's exchange of about  $1\text{eV}$ , a low spin ground state would necessitate an  $e_g$ - $e'_g$  splitting of more than  $5\text{eV}$ , in total disagreement with all experimental and theoretical results.

#### IV. DISCUSSION AND CONCLUSION

In the present work we determined the effective on-site and coupling parameters for the  $\text{Na}_{0.35}\text{CoO}_2 - 1.3\text{H}_2\text{O}$  compound from ab initio quantum chemical calculations properly treating both the strong correlation effects within the cobalt  $3d$  shell and the screening effects on the effective parameters. We determined the ligand field splitting as well as the on-site Coulomb repulsion and Hund's exchange within the Co  $3d$  orbitals. As far as the interactions between two cobalt atoms are concerned, we evaluated both the effective transfer integrals between the  $t_{2g}$  orbitals as well as the effective exchange. It is noticeable that, the ligand field splitting between the  $a_{1g}$  and  $e'_g$  orbitals resulting from the splitting of the  $t_{2g}$  orbitals is of the same order of magnitude (and even a little weaker) as the transfer integrals between two nearest neighbor Co atoms. In our opinion, both the  $a_{1g}$  and the  $e'_g$  orbitals should be taken into account in a proper description of this system.

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